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Analysis of Explosives in Soil Using Solid Phase Microextraction and Gas Chromatography

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Abstract: Current methods for the analysis of explosives in soils utilize time consuming sample preparation workups and extractions. The method detection limits for EPA Method 8330 for most analytes is substantially higher than the typical explosive concentrations encountered in soils near unexploded ordnance items, landmines, or other hidden explosive devices. It is desirable to develop new analytical techniques to analyze soil with low concentrations of explosives to support the development of explosive sensors. This report describes efforts to adapt headspace solid phase extraction and gas chromatography/mass spectrometry to provide a convenient and sensitive analysis method for explosives in soil.

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Current methods for the analysis of explosives in soils utilize time consuming sample preparation workups and extractions. The method detection limits for EPA Method 8330 for most analytes is substantially higher than the typical explosive concentrations encountered in soils near unexploded ordnance items, landmines, or other hidden explosive devices. It is desirable to develop new analytical techniques to analyze soil with low concentrations of explosives to support the development of explosive sensors. This report describes efforts to adapt headspace solid phase extraction and gas chromatography/mass spectrometry to provide a convenient and sensitive analysis method for explosives in soil.

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INTRODUCTION

Explosives are important chemicals, used in peaceful pursuits for construction and mining, and used for military purposes in a variety of forms. Explosives may be introduced into soil through dumping practices, as were formerly used during explosives' manufacturing processes, incomplete explosive bursts, and leaching from unexploded ordnance. Soils may need to be analyzed for explosives as a part of site characterization and monitoring to support site cleanup activities during environmental remediation of contaminated sites. Also, the detection and identification of explosives in soil may serve as clues to the presence of explosives from unexploded ordnance or landmines.

Soil analyses to support site cleanup are usually governed by the officially recognized EPA methods, Method 8330, Nitroaromatics and Nitramines by high performance liquid chromatography (HPLC), and Method 8095, Explosives by Gas Chromatography. The detection of explosives in soil as a clue to the presence of unexploded ordnance or landmines requires detection of explosives at much lower concentrations than are encountered in common site cleanup events. The special nature of explosive device detection through trace explosive signatures requires high sensitivity and near real-time response, and these tasks are usually best addressed with some type of near real-time chemical sensor. The development of sensors to detect trace explosives can be supported by a sensitive laboratory analysis method, even if the instrumental analysis response time is too slow to be useful as a field detection technique.

The defense advanced research projects agency (DARPA) conducted a research program to develop chemical detectors for explosives for use in detecting landmines, during its Dogsnose Program. Several detectors were developed to a prototype stage, with two technologies yielding particularly favorable results. Hibbs developed a detector based on nuclear quadrupole resonance (NQR) that was able to detect landmines filled with RDX explosive (Hibbs 2001). Landmines filled with TNT were successfully detected by quenching of fluorescence in an amplifying fluorescent polymer, developed by Wosnick and Swager (2000) and incorporated into the FIDO explosives detector by Cumming et al. (2001). The NQR sensors detect explosives through the NQR signal produced by solid explosive charges. The FIDO is an example of a trace explosive detector, which detects explosive devices by responding to vapor or solid particles often found in trace concentrations on the surface of landmines and other explosive devices. These sensors promise new technologies to improve the detection of landmines.

The small concentrations of explosives present as a clue to hidden explosives or landmines challenge even the most sensitive current explosives' detectors. A positive response raises the question of whether the response is a valid indication of the presence of explosives or if it is due to some interfering chemical. This is true whether the sensor is under development or is under

actual employment. There is need for sensitive confirmatory techniques that can be used to validate sensor response. Questions of the validity of response can best be addressed with a technique that is able to identify the actual chemical producing the response and provide information on the amount present.

The concentrations of explosives typically found on explosive devices are quite low, and challenge typical laboratory analyses such as liquid chromatography, gas chromatography, mass spectrometry, and other forms of spectroscopy. It is desirable to develop more sensitive techniques based on gas chromatography/mass spectrometry, to detect explosives and confirm the identities of the compounds responsible for positive explosive sensor response.

The promulgated method for environmental determination of explosives in soil used most commonly within the United States is EPA Method 8330. This method may be applied to soil or water samples, although somewhat different sample workups are used. EPA Method 8330 requires soil samples to be extracted with solvent under ultrasonic conditions for 18 hours, which precludes the use of this method or any variation to analyze samples rapidly. Method 8330 utilizes HPLC with detection by UV absorption (EPA 1996).

EPA Method 8095 utilizes gas chromatography with electron capture detection (GC/ECD) but the same sample workup and extraction procedures as EPA Method 8330. EPA Method 8095 anticipates significantly lower Method Detection Limits (MDLs) than does Method 8330, but the sample preparation times remain the same (EPA 2000).

Solid phase microextraction (SPME) is a sample extraction and preparation technique developed to extract organics from aqueous and gaseous samples and introduce them for analysis by gas chromatography, gas chromatography/mass spectrometry, and liquid chromatography. The technique involves short lengths of fused silica optical fiber, coated with sorptive polymeric coatings and packaged in syringe-like devices inside a septum-penetrating needle. When the device is inserted into a sample vial, the needle penetrates the septum and then the coated fiber is extended from the needle into contact with the sample. The coated fiber is exposed to the sample for a controlled interval, then it is withdrawn and the device is moved to the injection port of a gas chromatographer (GC) or gas chromatographer/mass spectrometer (GC/MS) or to an high pressure liquid chromatography (HPLC) interface, where the fiber is extended again into the carrier and the sorbed analytes desorb from the coated fiber into the mobile phase of the chromatographic system. The SPME technique, in combination with GC or GC/MS provides sensitive analyses since the entire sample extract is typically injected for analysis (Arthur et al. 1993; Chai and Pawliszn 1995; Zhang and Pawliszn 1993).

Barschick and Griest (1998) also studied explosives in seawater, using SPME prior to analysis with a gas chromatograph/ion trap mass spectrometer.

Furton et al. (2000) used similar SPME techniques in conjunction with solvent extraction to assist in the analysis of explosives from post-blast residue. They extracted the residues with an organic solvent and then exchanging the analytes into SPME fibers with the aid of salt water prior to analysis (Furton et al. 2000; Furton and Myers 2001). Calderera et al. (2003) studied the determination of explosives in water using SPME with GC/ECD analyses. Rodacy et al. (2000) studied combinations of SPME with IMS to analyze for explosives in sea water. Halasz et al. (2003) used SPME/GC/ MS to analyze samples of contaminated water for explosives.

Havenga and Rohwer (1999) described the use of headspace SPME and optimized conditions to analyze soils for a variety of PAH and other semivo-latile organic compounds, using GC/MS. Several workers have attempted to apply SPME to the detection and analysis of explosives in soil. Rodacy et al. (2000) devised a "lawn dart" sampler to expose SPME fibers to soils in situ for later analysis with an ion mobility spectrometer. Jenkins et al. (1999) prepared vials of soil with crystals of TNT embedded beneath a soil covering and used headspace SPME in conjunction with GC/ECD to detect vapor from TNT and impurities from military grade TNT. Cumming et al. (2001) used SPME/GC/ ECD to provide high sensitivity confirmation of explosives and related compounds from headspace over contaminated soils.

In this report we describe a headspace/SPME/GC/MS technique for the analysis of several of the EPA Method 8330 analytes from soil within an hour. Our initial investigations have examined the influence of several operational SPME variables upon the extraction technique, in an effort to optimize the extraction for explosives in soil. The investigation has focused on dry sand, minimizing effects from organic soil materials. Some of the variables examined include SPME exposure time, extraction temperature, and the effect of moisture.

METHODS

The GC/MS analyses were performed with a gas chromatograph interfaced with a quadrupole mass spectrometer (Hewlett Packard 5890/5971) con-trolled with a personal computer (Hewlett Packard Vectra 486/66XM) and DOS Chemstation software. The gas chromatograph was equipped with a split/splitless injection port equipped with a narrow bore, SPME liner (Supelco, Inc). The SPME experiments discussed were carried out using the 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) coated fibers in manual fiber holders and field sampler holders (Supelco, Inc). The GC/MS conditions used are summarized in Table 1.

The SPME sampling was carried out in 7 mL vials equipped with phenolic screw caps with holes and Teflon-faced silicone rubber septa. Initially a manually controlled sample heating block (Labline Multi-Blok, model 2050) was used to control the SPME temperature, although this was

Table 1. Summary of GC/MS conditions used.

Summary of method UXOSPME.M	
GC conditions	
Instrument:	HP-5890
Column:	Restek RTX-1701
Length:	30 m
Inner diameter:	0.25 mm
Phase thickness:	0.25 μm
Temperature program:	60°C (1 min)–240°C (9 min)@12°C/min
	240°C–270°C (0 min)@15°C/min
Injection temperature:	250°C
Injection liner:	0.75 mm SPME Liner
Inlet pressure	21 kPa (Constant)
Split flow	
Inlet purge delay:	5 min
Transfer line temperature:	280°C
MS conditions	
Instrument:	HP-5971
Solvent delay	0 sec
Scan range	35–350 Dalton
Scan rate	2.2 scans/sec
A/D duplicate readings	4
Ionization mode	EI
Ionization voltage	70 volts

replaced for later procedures with a digitally controlled heating block (Stable Temp, Cole Parmer, Inc.). The SPME procedures were carried out manually, with extraction times being monitored with a stopwatch.

The sampling was carried out on soil samples of Ottawa Sand (Science Grade, Fine White, Ward's Natural Science), which had been pretreated by heating to a temperature of 100°C overnight in a drying oven, and which was stored in the oven at that temperature until use. Samples (1 g) were weighed into vials before being spiked with solutions of the EPA Method 8330 and Method 8095 analytes. The analytes were obtained as commercial stock solutions (Restek) that were combined into a working stock solution, as listed in Table 2. The stock solutions were diluted with acetonitrile before being spiked into the soil samples. Varying amounts of the stock solution were used to obtain the desired concentrations in the spiked soil samples.

Samples were prepared by weighing 1 g aliquots of the Ottawa Sand into a vial and spiking the sand with the required volume of stock solution, using a gas-tight syringe. The required volume of water was then pipetted into the sand, using a settable automatic pipette (Rainin EDP) and the vial was

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Table 2. US EPA method 8330 analytes used, retention times, quantitation ions, and qualifier ions.

Name	R.T.	Target ion (m/Z)	Qualifier ion #1		Qualifier ion #2		Qualifier ion #3	
			Ion (m/Z)	Abundance vs. quant. ion (%)	Ion (m/Z)	Abundance vs. quant. ion (%)	Ion (m/Z)	Abundance vs. quant. ion (%)
Nitrobenzene (NB)	7.50	77.00	123	51	51	48	93	50
2-Nitrotoluene (2-NT)	8.32	120.00	65	93	91	58	92	55
3-Nitrotoluene (3-NT)	8.86	91.00	137	63	65	55	63	17
4-Nitrotoluene (4-NT)	9.14	91.00	65	80	137	76	63	24
Nitroglycerine (NG)	10.81	46.00	42	34	44	25	56	25
2,6-Dinitrotoluene (2,6-DNT)	12.43	165.00	89	54	63	53	91	37
1,3-Dinitrobenzene (DNB)	12.61	168.00	75	81	76	77	50	56
2,4-Dinitrotoluene (2,4-DNT)	13.36	165.00	89	66	63	41	90	23
ISTD-3,4-Dinitrotoluene (ISTD)	14.45	182.00	89	70	78	68	63	68
2,4,6-Trinitrotoluene (TNT)	15.53	210.00	89	50	63	40	76	20
1,3,5-Trinitrobenzene (TNB)	15.82	75.00	213	69	74	58	120	24
4-Amino-2,6-Dinitrotoluene (4-AM-DNT)	18.86	180.00	105	64	197	60	78	58
3,5-Dinitroanaline (3,5-DNA)	19.80	183.00	64	70	63	53	44	40
2-Amino-4,6-Dinitrotoluene (2-AM-DNT)	19.89	180.00	78	89	197	71	104	68
Tetryl	20.83	77.00	194	93	242	65	75	65

capped. The capped vial was then transferred to the heating block, the SPME fiber was inserted, and the SPME sampling period began. Following the extraction period the SPME fiber was withdrawn from the vial, transferred to the GC/MS injection port, and the GC/MS analysis run was started.

The GC/MS quantitative responses were monitored using the MS-DOS Chemstation software. Unless noted, quantitative responses were based on the peak areas for quantitation ions as listed in Table 2. Internal standards were used to decrease some of the effect on the quantitative responses from the sensitivity of the SPME procedure to experimental conditions. The actual internal standard used varied somewhat over the time of the experiments, and included 3,4-dinitrotoluene and Carbon-13 labeled 1,3,5-trinitrobenzene. Qualifier ions were used by the Chemstation software to ensure that quantitation ion response was due to the expected target compound.

In order to study the SPME parameters associated with this extraction method, the SPME sampling period was varied from 5–30 minutes. Water was suspected to be an important variable in the response of explosives by this technique, and varying amounts of water, from 50–250 μL, were added to the soil samples. The effect of temperature on the SPME response was studied by varying the heating block temperature between 80 and 120°C.

In effort to increase the sensitivity, a group of ions obtained from the electron impact ionization, and excerpted from those listed in Table 2, were used to devise a selected ion monitoring procedure. Ionization parameters and gas chromatographic procedures were used without change. The ion groups and dwell times used are listed in Table 2.

RESULTS

A total ion chromatogram from a typical SPME/GC/MS analysis made from a spiked sand sample is shown in Fig. 1. A strong response was obtained for most of the analytes. Two analytes, 2-aminodinitrotoluene and 3,5-dinitroaniline eluted very close to each other despite attempts to minimize coeluting compounds, but these substances exhibited different mass spectra and it was possible to designate quantitation ions that were distinct for each substance. In some runs, sufficient acetonitrile remained when the vial was capped to produce a mild solvent peak response as can be seen in Fig. 1. These conditions were judged to be adequate to study the SPME responses while attempting to optimize the extraction procedure.

Figure 2 shows a plot of the responses, normalized to the internal standard response, as temperature was varied. Here, the peak area for the selected ion profile of the quantitation ion and for the largest peak within a reasonably small retention time window for each target peak was used to calculate the response. The raw area was corrected by subtracting the peak area for the analyte peak in a blank run composed of clean sand prepared in the same manner as the spiked sample. Where appropriate quantitation ions were
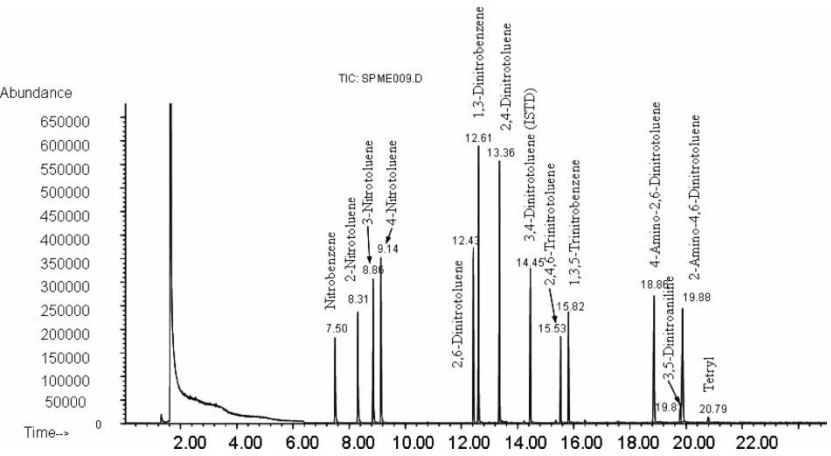
Figure 1. Typical total ion chromatogram (TIC) from SPME/GC/MS of EPA Method 8330 analytes spiked in Ottawa sand. This sample was spiked at a concentration of 18 μg TNT/g sand.

selected and correct retention times, there were no positive blank responses to subtract. The response of an analyte was taken to be the corrected area for a given analyte divided by the quantitation ion peak area for the selected internal standard. The authors had expected a simple improvement in response as temperature was increased, due to the low vapor pressure of the
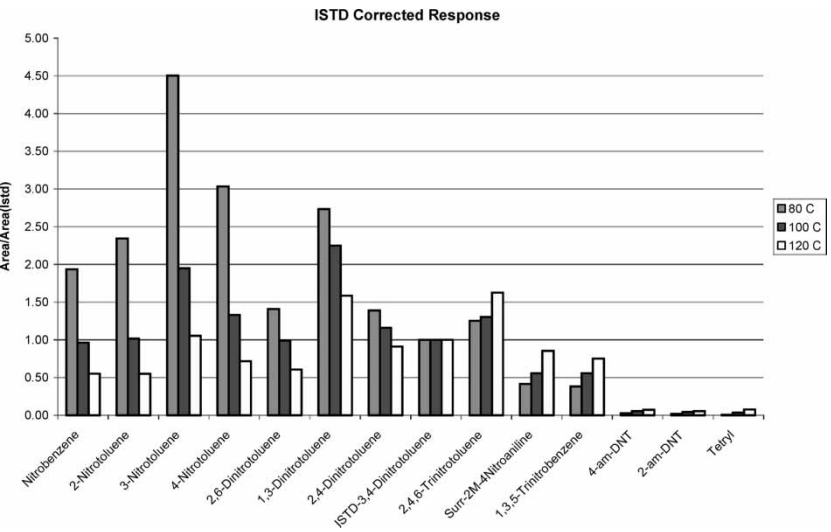

Figure 2. Effect of temperature on SPME/GC/MS response of explosives in Ottawa sand.

explosive compounds. Instead, only certain of the low volatility analytes exhibited improved responses as the temperature increased. More volatile analytes exhibited lower normalized response to increasing temperature. From these responses, due to our interest in explosives, and using the behavior of TNT as an important typical explosive, many of the subsequent SPME procedures were done with the sample heated to 110°C.

Added water was found to improve the response from analytes with volatilities greater than or equal to nitroglycerine, although the effect was slight. More volatile analytes showed little effect with the added moisture.

The required SPME exposure time was investigated by varying the extraction period between 5 and 30 minutes. Again, the response was analyte dependent, as shown in Fig. 3. The more volatile analytes tended to favor extended SPME extraction times. Although several compounds showed reduced response for the 15-minute extraction period, extractions for 20 minutes for these compounds continued the trend of increased response, up to the limit studied. Analytes with lower volatilities tended to favor lower extraction periods. The response for TNT favored extraction periods from 15–30 minutes, with the best response at 15 minutes.

The responses did not favor a single set of conditions. Due to the importance of TNT as a military explosive and potential interest in environmental site surveys, most subsequent experiments were performed under conditions that favored TNT. These conditions were extraction in vials loaded with 200 µL of water, at 110°C, for 15 minutes. With conditions favoring TNT, samples of sand spiked with varying concentrations of the analytes
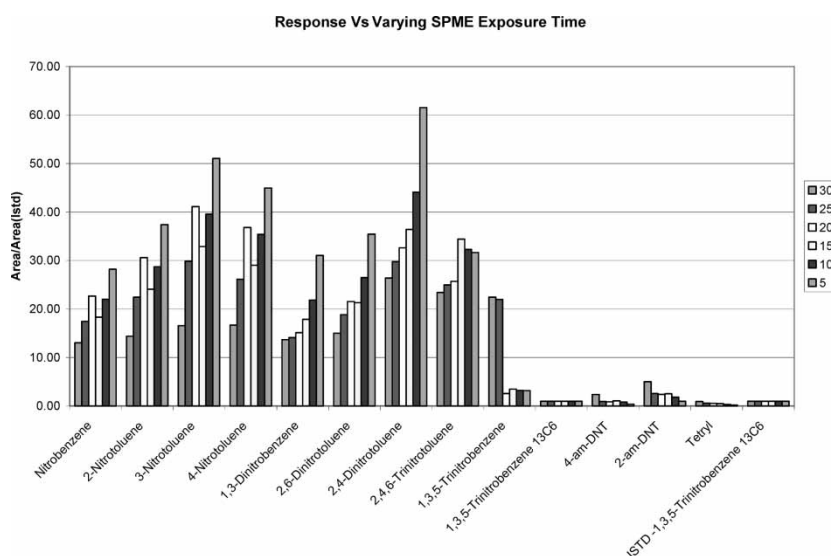

Figure 3. Effect of varying SPME exposure time.

yielded responses for TNT that were linear from concentrations of 0.7–64 μg TNT/g sand. Other analytes responded with linear trends of response vs. concentration over more restricted ranges. For most of the analytes, the response for the response became strongly nonlinear at concentrations of 50–60 μg/g. The response for TNT obtained by scanned, target ion detection, relative to an internal standard of 3,4-dinitrotoluene, is shown in Fig. 4.

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) were included in the standard solutions prepared, but they were not detected using any of the conditions studied. These compounds remain a challenge for GC and GC/MS detection and analysis.

DISCUSSION

The SPME conditions for this analysis must be carefully controlled if the results are to be used for quantitative information. Temperature and SPME exposure time strongly control the results and the moisture content controls response to a lesser degree. The effect of moisture was initially expected to be a stronger factor, but the results obtained do not support this. More volatile analytes, up to nitroglycerine, favored higher moisture content, but the effect is small. From this, moisture in soil samples should have little effect in the results obtained from suspected contaminated sites, and it should be possible to analyze such samples before drying, avoiding the risk of any loss of volatile analytes during the drying process. The soil aliquots may be weighed after the SPME procedure is complete to obtain the dry weight of the samples if that is needed.
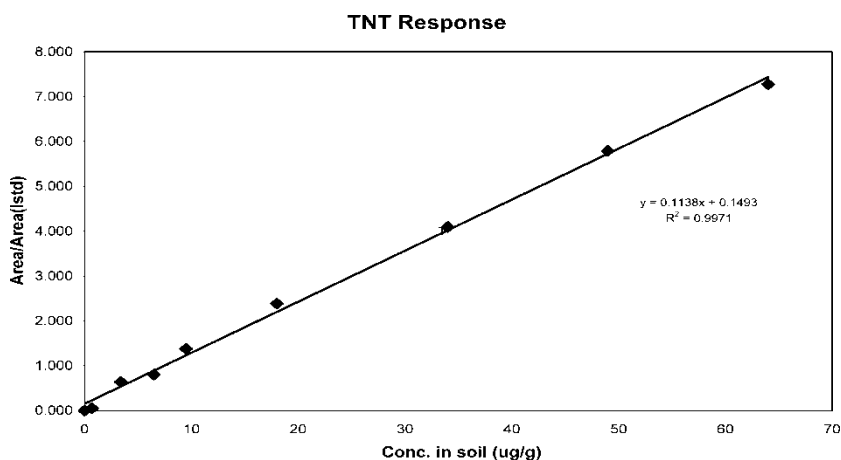

TNT Response

$y = 0.1138x + 0.1493$
$R^2 = 0.9971$

Figure 4. Target ion quantitative response plot for TNT vs. 3,4-DNT as an internal standard.

Temperature was found to be a stronger control on the quantitative SPME/GC/MS response. Increasing the SPME extraction temperature favored the response from the less volatile analytes. The need for greater temperature control prompted the change from using a heated block with a simple analog control to a block with a digital temperature control for greater precision in controlling the SPME temperature.

The length of the SPME extraction period was found to be another strong controlling factor of the response strength. Several of the more volatile analytes exhibited decreasing response as the extraction time increased, indicating those compounds may have partially escaped from the extraction vial over the time of the procedure. Tetryl exhibited stronger response as the SPME extraction period increased, and 30 minutes, the longest time investigated, may not have been long enough to maximize the response for tetryl. Even when the SPME procedure was performed for 30 minutes, the response from tetryl was not strong, so lengthening the exposure time to increase the response was not beneficial. The response for TNT maximized with 15 minutes of exposure time, and this was used for several of the subsequent procedures.

DISCLAIMER

Certain instruments and software have been identified by brand name to fully document the work. Such mention does not imply recommendation or endorsement by the Air Force nor does it imply that the items identified are the best available for the purpose.

REFERENCES

Arthur, C.L., Chai, M., and Pawlizyn, J. 1993. Solventless injection technique for microcolumn separations. *J. Microcolumn Sep.*, 5 (1): 51–56.

Barshick, S.A. and Griest, W.H. 1998. Trace analysis of explosives in seawater using solid-phase microextraction and gas chromotography/ion trap mass spectrometry. *Anal. Chem.*, 70 (14): 3015–3020.

Calderara, S., Gardebas, D., and Martinez, F. 2003. Solid phase micro extraction coupled with on-column GC/ECD for the post-blast analysis of organic explosives. *Forensic Sci. Int.*, 137: 6–12.

Chai, M. and Pawliszn, J. 1995. Analysis of environmental air samples by solid-phase microextraction and gas chromatography/ion trap mass spectrometry. *Environ. Sci. Technol.*, 29 (3): 693–701.

Cumming, C.J., Aker, C., Fisher, M., Fox, M., la Grone, M.J., Reust, D., Rockley, M.G., Swager, T.M., Towers, E., and Williams, V. 2001. Using novel fluorescent polymers as sensory materials for above-ground sensing of chemical signature compounds emanating from buried landmines. *IEEE T. Geosci. Remote*, 39 (6): 1119–1128.

EPA. Method 8330. 1996. *Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)*. SW-846 on CD-ROM US Environmental Protection Agency, Office of Solid Waste, Available from NTIS, May.

EPA. Method 8095, 2000. *Explosives by Gas Chromatography*, US Environmental Protection Agency. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8095.pdf, Revision 0, November.

Furton, K.G. and Myers, L.J. 2001. The scientific foundation and efficacy of the use of canines as chemical detectors for explosives. *Talanta*, 54: 487–500.

Furton, K.G., Almirall, J.R., Bi, M., Wang, J., and Wu, L. 2000. Application of solid-phase microextraction to the recovery of explosives and ignitable liquid residues from forensic specimens. *J. Chromatogra. A*, 885: 419–432.

Halasz, A., Groom, C., Zhou, E., Paquet, L., Beaulieu, C., Deschamps, S., Corriveau, A., Thiboutot, S., Ampleman, G., Dubois, C., and Hawari, J. 2003. Detection of explosives and their degradation products in soil environments. *J. Chromatogr. A*, 963: 411–418.

Havenga, W.J. and Rohwer, E.R. 1999. Chemical characterization and screening of hydrocarbon pollution in industrial soils by headspace solid-phase microextraction. *J. Chromatogr. A*, 848: 279–295.

Hibbs, A.D. 2001. *In-situ Real Time Detection of Explosive/Chemical Compounds in Mines Using Nuclear Quadrupole Resonance (NQR)*. Technical Report No. ADA388897, Defense Technical Information Center (DTIC).

Jenkins, T.F., Leggett, D.C., Ranney, D.C., and Vapor, T.A. *Signatures from Military Explosives Part 1. Vapor Transport from Buried Military-Grade TNT*. Special Report 99-21, Engineering Research and Development Center: Hanover, NH, December.

Rodacy, P.J., Walker, P.K., Reber, S.D., Phelan, J., and Andre, J.V. 2000. Explosive Detection in the Marine Environment and On Land Using Ion Mobility Spectroscopy A Summary of Field Tests. Technical Report SAND2000-0921, Sandia National Laboratory: Albuquerque, NM, April 27.

Wosnick, J.H. and Swager, T.M. 2004. Molecular photonic and electronic circuitry for ultra-sensitive chemical sensors. *Curr. Opini. Chem. Biol.*, 4: 715–720.

Zhang, Z. and Pawliszn, J. 1993. Analysis of organic compounds in environmental samples by headspace solid phase microextraction. *J. High Res. Chromatogr.*, 16: 689–692.